ELECTRICAL RESISTIVITY OF NATURAL DIAMOND AND DIAMOND FILMS BETWEEN ROOM TEMPERATURE AND 1200 C: STATUS UPDATE

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ABSTRACT

The electrical resistivity of diamond films has been measured between room temperature and 1200 C. The films were grown by either microwave Plasma CVD or combustion flame at three different places. The resistivities of the current films are compared to those measured for both natural IIa diamond and films grown only one to two years ago, A dramatic increase in the resistivities of the current films is observed and reported here. Some pitfalls of high temperature resistivity measurements such as surface reconstruction and graphitization will also be discussed.

INTRODUCTION

The electrical resistivity of natural insulating type IIa diamond is very high with room temperature values of 10^{16} Ω-cm quoted in the literature, However, it has been shown by Vandersande and Zoltan [1] that this value is the "apparatus-limited" resistivity, i.e. higher resistivity values cannot be measured. The actual room temperature resistivity of type IIa diamond is considerably higher than 10^{16} Ω-cm. Up until about a year ago, the room temperature resistivity of diamond films has typically been in the 10^8 to 10^{15} Ω-cm range [1, 2, 3, 4] and the resistivity of most of the films equalled that of natural type IIa diamond only at the highest temperatures (typically 800-1200 C), During the past year or so the quality of the best diamond films has improved considerably and as a result the electrical resistivities have increased, Results of measurements on several of such films are presented here. Diamond films with resistivities greater than that of natural type IIa diamond can now be grown.

Electrical resistivity measurements of insulators at high temperatures are not simple and especially with diamond there are numerous pitfalls that are specific to diamond. Several of the pitfalls will be discussed below and precautions and techniques to avoid them will be given.

EXPERIMENTAL

An apparatus was specifically designed and built to be able to measure very high resistivity insulators up to at least 1200 C. This apparatus is discussed in detail elsewhere [1]. Very briefly, the resistivity is measured perpendicular through the sample which sits in an alumina holder. The top and bottom electrodes are iridium foil pressed against the sample. This type of electrode configuration does result in ohmic behavior in the range of voltages used (+100 V to -100 V). originally, a guard ring was used on the larger samples but it was found that identical results were obtained without one on the heating curve up to 1200 C as long as the data was taken within a period of several hours. This result made it possible not to use guard rings since it is very difficult to put them on the small and irregularly shaped samples. The vacuum in the, test station was 10s to 10 ^{6} Torr.

The diamond films were supplied by several different sources. The Crystallume sample was a free standing clear, colorless film 300 μm thick grown by microwave plasma CVD using their high purity technique. The Norton sample was a free standing greyish film 1.1 mm thick grown by their CVD process. The North Carolina State University (NCSU) samples were grown using two different techniques; two samples of 20 μm thickness were grown on a silicon substrate using a combustion flame technique [5] while two others were 5,5 μm and 9 μm thick on a silicon substrate grown by downstream microwave plasma CVD [6]. The samples were measured in the as received condition. The Crystallume and Norton samples were heat treated and cleaned after growth wheras the NCSU samples were not.

EXPERIMENTAL RESULTS AND DISCUSSION

The electrical conductivity versus inverse temperature between room temperature and 1000-1200 C for the Crystallume and Norton and NCSU films arc shown in figures 1 and 2 respectively. The conductivity of natural type IIa diamond is shown for comparison. The conductivity of this natural diamond is approximately constant in the 1O ^{15} -1016 $\Omega^{-1}cm^{-1}$ range between room temperature and 200 C. This is the "apparatus-limited" value which is the lowest conductivity the apparatus will measure and represents leakage currents around the sample through the holder [1]. The Crystallume and Norton samples also show this "apparatus-limited" value with the former having this value up to 300 C and the latter up to about 130 C. These two films thus both have resistivities that would be expected to be greater than 10^{16} Ω-cm at room temperature. "l'his is a great improvement over samples grown only a year ago. The Crystallume sample has a conductivity y lower (a resistivit y higher) than that for the natural t ypc 11a di amend over the whole temperature range. This sample has the highest resistivity measured up until now and the result indicates that this polycrystalline high purity diamond film has less defects and is thus purer than a good quality single crystal type IIa diamond. The Norton sample was not made with purity in mind but was made for thickness. It was thus less pm-c than the Crystallume sample and the natural diamond and as a result has a slightly higher conductivity in the 150-1000 C range. The activation energies of these two films and the natural IIa diamond arc all three in the 1.55 ± 0.03 CV range. This energy is believed to be associated with substitutional nitrogen or the di-nitrogen [7].

The two NCSU combustion flame samples have slightly higher conductivities in the room temperature to 400 C range but either have a lower conductivity or the same conductivity as that for the natural type IIa diamond between 400 C and 1200 C. One of these films has approximately the same conductivity as the Crystallume sample in the 500 -1000 C range indicating that the quality of combustion flame samples has improved considerably during the past year as WC]].

MEASUREMENT PITFALLS

The high temperature electrical resistivity measurement of natural diamond and diamond films is not as simple as with other insulators such as sapphire because of the changes that take. place on the diamond surface. A restructuring of the diamond surface takes place from about 900 C to 1050 C [8, 9] and results in "graphitization" (non-diamond carbon) of the surface. Onc theory is that the hydrogen, that is bonded to the surface carbon atoms, is driven off (dehydrogenation) and that the surface carbon atoms then collapse in a mm-diamond form of carbon. This layer would be slightly conducting which would lead to surface conduction between the two electrodes resulting in a higher conductivity. The effect on the conductivity of the cooling curve (down from 1000 C back to room temperature) can clearly be seen in figure 1 for the Norton sample. The conductivity starts to become higher than on the heating curve at about 800 C and at room temperature is five orders of magnitude higher than before the measurement. Cleaning the sample in an acid solution restores the original resistivity value and then measuring the conductivity up to 1000 C results in the identical data as the first time.

Another type of "graphitization" occurs by heating the diamond surface up to over about 400 C. It appears that in our vacuum of 10^{5} - 10^{6} Torr the oxygen attacks the surface and forms Co and Co_2 (oxidation). '1'hen, when onc or both of these come off the surface, "graphitization" (non-diamond carbon) of the, surface takes place with the resultant surface conduction path, Cooling the sample back down to room temperature now results in a higher conductivity. Cleaning the sample again results in the original conductivity. '1'here is evidence that even in a vacuum of 1010 Torr some surface "graphitization" takes place as low as 450 C [JO]. This layer is not optically visible and was only detected by LEED [10].

Leaving the Crystallume sample for 16 hours at between 400 and 480 C in our vacuum resulted in the conductivity rising about three orders of magnitude above the original conductivity y curve. This is shown in figure 3. Heating the sample to higher temperatures then resulted in the conductivity approaching the original conductivity at the highest temperatures. It appears that some or most of the "graphite" layer formed as a result of oxidation is driven off at higher temperatures. There is evidence that the thermal desorption of CO takes place at about 600 C [8]. Then once above 900 C reconstruction of the surface takes place and graphitization occurs again. The cooling curve now has a much higher conductivity y (about 10 orders of magnitude), probabl y as a result of the combined "graphitization effects. " These results thus clearly show that the data must be taken relatively quickly above 400 C. in our case, it takes about two hours to go from 400 to 1200 C.

A guard ring configuration was used on the Norton sample for onc of the measurements and it was found that the heating data was identical to the case of no guard ring. However, it was found that with the guard ring the reconstruction/graphi tization effect on the conductivity on the cooling curve was reduced significantly, as expected. The conductivity was now only onc to two orders of magnitude higher at room temperature. In most cases, it is not possible to usc a guard ring configuration because of the small size or odd sampe of the sample. Also, most literature reported measurements that only go up to 400-500 C did not usc a guard ring because it was not believed that graphitization takes place at those temperatures. As is clearly shown here, that is a mistaken belief that will result in incorrect data, especially on the cooling curve.

Adsorbed hydrogen (the activated species which is different from the bonded hydrogen) coming off the surface has a different effect on the conductivity than the surface bonded hydrogen. The conductivity was found to be approximately linear between room temperature and 300 C and then follows the curve for natural type IIa diamond. This is shown in figure 4 for a NCSU film grown by CVD. On the cooling curve the conductivity falls below the original value by six orders of magnitude. The lower conductivity is thus the real resistivity of the film. The adsorbed hydrogen clearly has a pronounced effect and underestimates the resistivity of the film if only room temperature values are measured. The exact same effect and conductivity behavior was observed on another NCSU film grown by CVD. Numerous results in the literature probably only represent the room temperature resistivity of a non-cleaned film which thus gives for too low a resistivity value due to the adsorbed hydrogen. It is very interesting to note that the rc-heating and subsequent cooling curve fall right on top of the first heating (above 300 C) and cooling curves. This was repeated on the second sample as well. It appears that reconstruction of the surface does not take place for these two samples. It is not clear why not and it needs more work to understand exactly what is happening.

CONCLUSION

The resistivity of some of the best diamond films between room temperature and 1200 C is now higher than that for single crystal good quality type IIa diamond over all or part of the temperature range. This is a significant improvement over the electrical resistivity of diamond films grown only a year ago. The results also show that high temperature resistivity measurements can be used to determine the purity of diamond films. "Graphitization" (non-diamond carbon) of the diamond surface duc to oxidation can start as low as 400 C while "graphitization" duc to reconstruction starts at around 900 C. Both these can affect the conductivity results.

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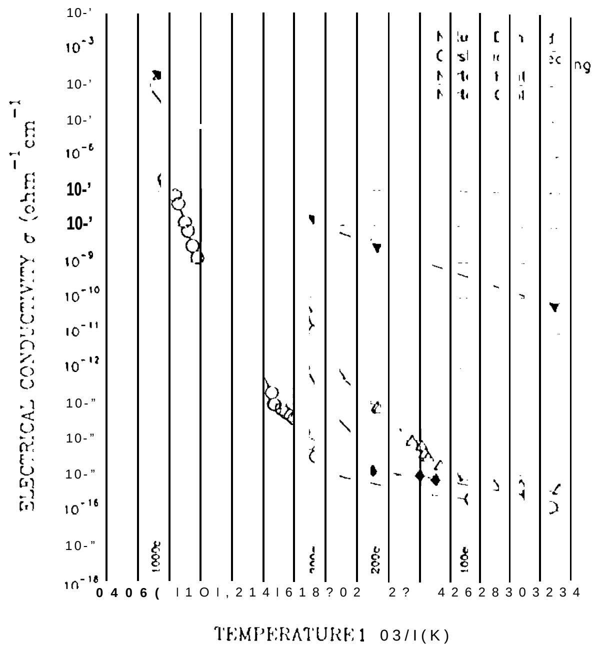

Figure 1: The electrical conductivity of CVD grown Crystallume and Norton diamond films. The conductivity of single crystal natual type IIa diamond is shown for comparison. The cooling curve for the Norton sample is also shown.

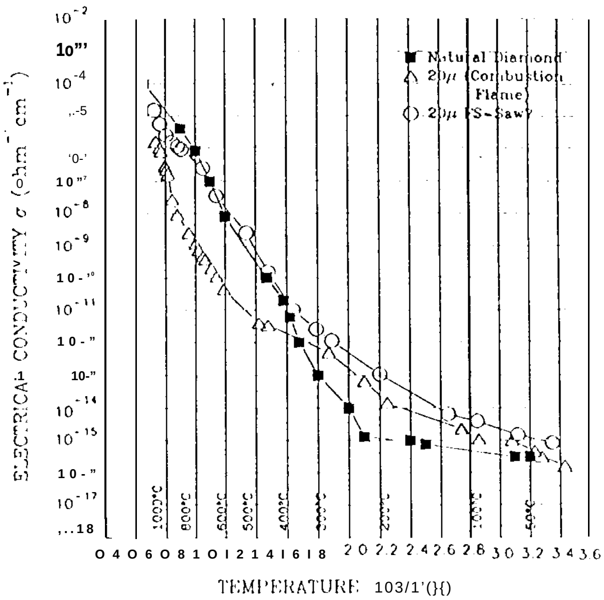

Figure 2: The electrical conductivity of the two NCSU combustion flame grown diamond films of 20 μm thickness. The conductivity of single crystal natural type IIa diamond is shown for comparison.

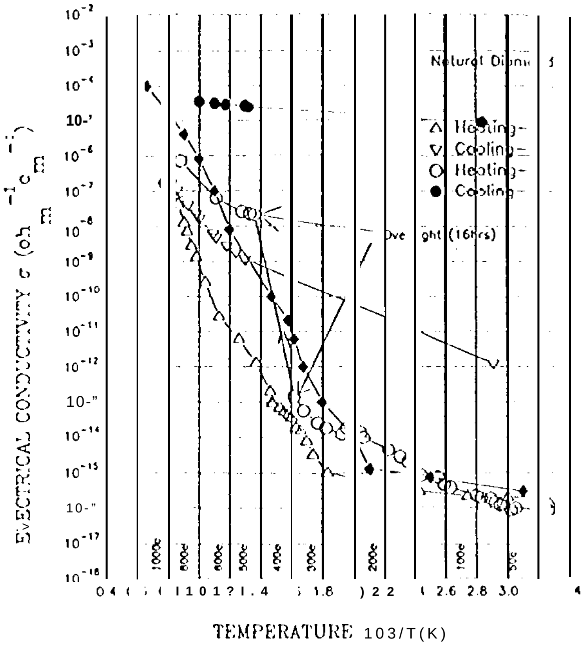

Figure 3: The electrical conductivity of the 300 μm thick Crystallume sample. The heating-1 curve was taken with our normal data taking speed while the heating-2 curve was taken much slower and held overnight at 480 C for 16 hours. The effect of "graphitization" (non-diamond carbon) can clearly be Seen.

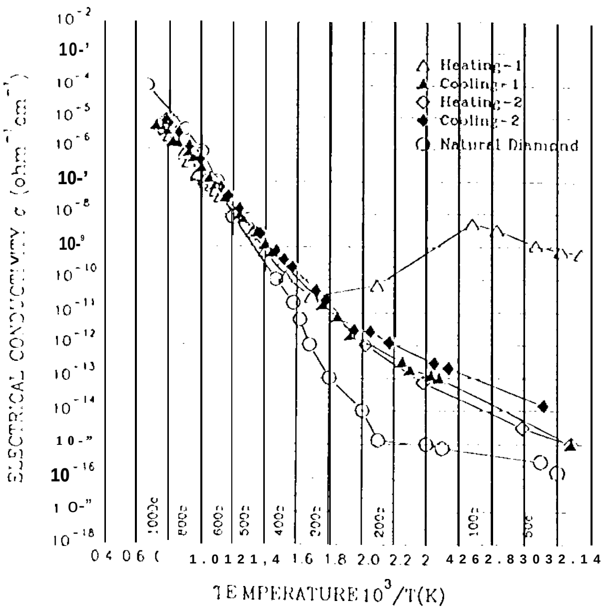

Figure 4: The electrical conductivity of a NCSU CVD grown 9 μm thick diamond film. The heating-1 curve up to 300 C (constant conductivity) is believed to be related to adsorbed hydrogen leaving the film surface.